PentaBDE Alternatives in Homes, Offices and Cars

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Introduction

PentaBDE was phased out of production in the USA in 2004 and was recently added to the Stockholm Convention. Nevertheless, large quantities remain in use in polyurethane foam furniture in North America. At least two major replacements for pentaBDE are used in the USA. Firemaster 550 (FM550) consists of approximately 50% triphenyl phosphate (TPP) and isopropylated triaryl phosphate and 50% brominated flame retardants. We previously identified the two brominated components as bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) (Stapleton et al 2008b). TBPH has also been used separately as a product called DP-45, e.g., in wires and cables containing polyvinylchloride. A second major pentaBDE replacement is tris(1,3-dichloro-2-propyl) phosphate (TDCPP). TDCPP and TPP have been used for decades as flame retardants or plasticizers (TPP only) in a wide variety of applications (Stapleton et al 2009a). As discussed elsewhere at this meeting, TDCPP is fairly well metabolized in humans; TDCPP or its metabolites may be developmentally neurotoxic (Stapleton et al 2010). We recently reported on the presence of pentaBDE replacements in house dust as well as foam samples (Stapleton et al 2008b, 2009a). However, no data are available on the concentrations of these compounds in dust from offices or cars. As fire codes can be stricter for office furniture than for residential furniture, dust concentrations of pentaBDE and its replacements may be higher in offices than homes. Furthermore, no data are available on time trends of these compounds in dust. We therefore collected dust from homes, offices and cars in the Boston, MA area and compared our results with our earlier work. In these offices we also collected air samples and handwipes.

Materials and Methods

In the winter of 2009 we sampled the homes, offices and cars of 31 participants in the Boston area. Dust samples were collected using a cellulose extraction thimble (Whatman International) inserted between the crevice tool and vacuum tube extender of a Eureka Mighty-Mite vacuum cleaner (Allen et al 2008). Each home main living area (MLA) and office was vacuumed for approximately 10 minutes, capturing dust from the surface area of the room. Vehicles were vacuumed for approximately 10 minutes, collecting dust from the entire surface of the front and back seats. The dashboard, floor, and other surfaces of the vehicles were not vacuumed. Dust samples were sieved to collect particles <500 μm in size. The sieved samples were then placed in clean amber glass jars and stored at -20°C. Sodium sulfate powder was used as a surrogate for dust in the collection of field blanks.

Handwipe samples were collected from each participant in their office environment at least 60 minutes after they had last washed their hands. A sterile gauze pad was immersed in 3 ml of isopropyl alcohol

and then used to wipe both the palm and back of hand from wrist to fingertips. Left and right hand samples were analyzed together, providing one measurement per participant. A field blank wipe sample was paired with the collection of each handwipe sample by soaking a gauze pad in isopropyl alcohol and placing it directly into the glass vial (Stapleton et al., 2008a).

Indoor air was collected from the offices using active sampling. We used a glass-fiber filter followed by a pre-cleaned polyurethane plug; air was sampled for approximately 48 hours at 4 L/min.

Samples were analyzed for PBDEs, TBPH, TBB, TCDPP and TPP using gas chromatography-mass spectrometry as previously described (Allen et al. 2007; Stapleton et al., 2008a, 2008b, 2009a). Samples were blank-corrected using the mean of the field blanks and concentrations below the LOD were substituted with a value of ½ the LOD. All data were log-transformed; statistical analyses were performed using SAS version 9.1 and Microsoft Excel. For the purposes of this paper, pentaBDE was defined as the sum of congeners 28/33, 47, 49, 66, 75, 85/155, 99, 100, 138, 153 and 154. OctaBDE was defined as congeners 183, 196, 197, 201 and 203. For decaBDE, we used the most prominent congener, BDE209. PBDE congeners detected at >50% in samples were included in statistical analyses and were found to be correlated within congener groups.

Results and Discussion

Comparison of 2009 dust samples between home, office and car

Dust concentrations of PBDEs and alternative flame retardants from the homes, offices and cars of the present study (collected in 2009) are presented in the first three columns of Table 1. About one third of participants in our study did not have a car, limiting the number of car dust samples to 20. The statistical power of some comparisons was also limited by some large geometric standard deviations (data not shown). Concentrations of alternative flame retardants in dust were similar to or exceeded (particularly TDCPP in cars) the concentrations of pentaBDE. Concentrations of pentaBDE were somewhat lower in the main living area (MLA) of homes compared with offices and cars, but the differences were not statistically significant. OctaBDE (often used in office equipment) and BDE209 were significantly higher in office dust compared with homes. TBPH, a component of FM550 (one pentaBDE alternative), was significantly elevated in offices vs. homes. While there were no significant differences for TBB, concentrations of this compound were significantly correlated with TBPH, suggesting that the predominant source is FM550. The increased presence of TBPH in offices may be due to three factors: 1) Many offices in this study contained furniture purchased since 2004; 2) Unlike homes, furniture used in offices in Boston, MA is generally required to meet California fire retardancy standards; 3) Increased use in offices of wires and cables treated with DP-45. TDCPP was significantly elevated in cars compared with homes (with a maximum value approaching 1 mg/g), although this may be partly due to differences in the way dust was sampled (car seats vs. room surfaces). In sum, our data suggest higher concentrations of pentaBDE alternative in offices (particularly TBPH) and cars (particularly TDCPP) compared with homes.

We are not aware of any other published data on pentaBDE alternatives in automobiles. The PBDE concentrations reported by Lagalante et al (2009) are similar to our own on a congener-specific basis (data not shown). The cars in our study were primarily foreign in make with a median production year

of 2001.

Potential time trends

In 2006, dust from the main living areas of 20 other Boston homes were sampled and analyzed using the same collection methods and laboratory; these homes were sampled twice, six to eight months apart (Allen 2008). As shown in Table 1, concentrations of pentaBDE in these homes were significantly higher than the homes we sampled in 2009. While this suggests a downward trend in pentaBDE concentrations—consistent with the phaseout of 2004 (and assuming some turnover in furniture)—we cannot rule out differences due to sampling: both sets of participants (2006 and 2009) were convenience samples. Similarly, TBPH was significantly higher in the 2009 samples compared with the 2006 samples, but this may be partly due to differences in extraction efficiency and recovery of TBPH with slightly different extraction methods.

TDCPP was not measured in the 2006 samples. However, TDCPP was measured in dust collected between 2002-2007 from 50 other Boston-area homes (Stapleton et al 2009a). The geometric mean concentration of TDCPP in the 2002-2007 dust samples was 1890 ng/g, significantly less than our MLA dust from 2009: 6307 ng/g. This suggests that TDCPP dust concentrations may have increased over time in house dust. However the comparison is complicated by the difference in methods of dust collection: the 2002-7 dust was sieved to a different size fraction (<150 μm) and collected from home vacuum cleaner bags, a method that can differ from investigator-collected dust, at least for PBDEs (Allen et al 2008). More research is needed on time trends of flame retardants in dust.

Handwipes

PBDE levels in handwipes and their relationship to serum and dust concentrations are discussed elsewhere at this meeting (Watkins et al 2010). We report here preliminary analyses for levels of TBPH and TBB. TBPH was detected in only 23% of handwipe samples (LOD=0.25 ng), but these results are limited by matrix interference. TBB was detected in 100% of samples with a geometric mean of 116 ng. There was a highly significant correlation between TBB levels on handwipes (collected in the office) and concentrations in dust from participant's offices (r=0.65, p=0.0001). This suggests that offices are a major source of the TBB found in these handwipe samples. We have also found a moderate correlation between pentaBDE on handwipes and office dust (Watkins et al 2010). As pentaBDE and TBB were not correlated within dust samples (or handwipe samples), the dust-handwipe associations for each compound are independent. These data suggest that hand-to-mouth activity may be an important route of exposure (Stapleton et al. 2008a).

Office Air

PBDEs (excluding BDE 209) were log-normally distributed in these samples of office air with a geometric mean of 478 pg/m^3. TBB and TBPH were detected in 39 % (LOD=16 pg/m^3) and 13 % (LOD=13 pg/m^3) of samples, respectively. In preliminary results, we detected TDCPP in 87% of offices with a geometric mean of 1.2 ng/m^3. We are not aware of other indoor air data on TDCPP for North America, but our results appear roughly comparable with results from other countries (Stapleton et al 2009b).

In sum, our results suggest that homes, offices and cars should all be considered when examining exposure to PBDEs and alternative flame retardants. Concentrations of alternative flame retardants in dust were similar to or exceeded the concentrations of pentaBDE.

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Table 1. Dust Concentrations, Geometric Means (ng/g)

	MLA 2009 (n=30)	Office 2009 (n=31)	Car 2009 (n=20)	MLA 2006-1 (n=20)	MLA 2006-2 (n=19)
pentaBDE	1918	2591	2950	5454*	5149*
octaBDE	78	232*	184	51	130
BDE209	1534	4127*	4651	4502	3527
TBB	248	225	295	--	322
TBPH	923	2037*	1068	--	234*
TDCPP	6307	9778	26105*	--	--
TPP	4496	4098	3070	--	--

* Significantly different ($p < 0.05$) from MLA 2009, the main living area of the home (reference group)